

THE INVESTIGATION OF MAGNESIUM PERCHLORATE/IRON PHASE-MINERAL MIXTURES AS A POSSIBLE SOURCE OF OXYGEN AND CHLORINE DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT IN GALE CRATER, MARS. B. Sutter^{1,2}, E. Heil^{1,2}, P.D. Archer^{1,2}, D.W. Ming², J.L. Eigenbrode³, H.B. Franz³, D.P. Glavin³, A.C. McAdam³, P.R. Mahaffy³, P.B. Niles², J.C. Stern³, R. Navarro-Gonzalez⁴, C.P. McKay⁵ and the MSL Science Team. ¹Jacobs, Houston, TX 77058, ²NASA Johnson Space Center, Houston TX 77058, ³NASA Goddard Space Flight Center, Greenbelt, MD 20771, ⁴Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, ⁵NASA Ames Research Center, Moffett Field, CA 94035.

Introduction: The Sample Analysis at Mars (SAM) instrument onboard the Curiosity rover detected O₂ and HCl gas releases from the Rocknest (RN) eolian bedform and the John Klein (JK) and Cumberland (CB) drill hole materials in Gale Crater (Fig. 1) [1,2]. Chlorinated hydrocarbons have also been detected by the SAM quadrupole mass spectrometer (QMS) and gas chromatography/mass spectrometer (GCMS) [1,2,3,4]. These detections along with the detection of perchlorate (ClO₄⁻) by the Mars Phoenix Lander's Wet Chemistry Laboratory (WCL) [5] suggesting perchlorate is a possible candidate for evolved O₂ and chlorine species. Laboratory thermal analysis of individual perchlorates has yet to provide an unequivocal temperature match to the SAM O₂ and HCl release data [1,2]. Catalytic reactions of Fe phases in the Gale Crater material with perchlorates can potentially reduce the decomposition temperatures of these otherwise pure perchlorate/chlorate phases [e.g., 6,7]. Iron mineralogy found in the Rocknest materials when mixed with Ca-perchlorate was found to cause O₂ release temperatures to be closer match to the SAM O₂ release data and enhance HCl gas releases. Exact matches to the SAM data has unfortunately not been achieved with Ca-perchlorate-Fe-phase mixtures [8]. The effects of Fe-phases on magnesium perchlorate thermal decomposition release of O₂ and HCl have not been evaluated and may provide improved matches to the SAM O₂ and HCl release data. This work will evaluate the thermal decomposition of magnesium perchlorate mixed with fayalite/magnetite phase and a Mauna Kea palagonite (HWMK 919). The objectives are to 1) summarize O₂ and HCl releases from the Gale Crater materials, and 2) evaluate the O₂ and HCl releases from the Mg-perchlorate + Fe phase mixtures to determine if Mg-perchlorate mixed with Fe-phases can explain the Gale Crater O₂ and HCl releases.

Materials and Methods: The Rocknest material examined by SAM consists of unconsolidated sand and dusty material [1]. John Klein and CB are drill hole samples (~6 cm deep) derived from the Sheepbed mudstone and are 3 m and 10 cm apart, horizontally and vertically, respectively [2]. The < 150- μm size fraction was examined by SAM. Samples were heated (35 °C min⁻¹) from 45 to ~860°C in a 25 mb He purge

at ~0.8 sccm. Evolved gases were analyzed by the SAM-QMS over the entire temperature range.

A laboratory Setaram Sensys-Evo differential scanning calorimeter (DSC) coupled to a Stanford Research Systems Universal Gas Analyzer at Johnson Space Center (JSC) were configured to operate similarly to the SAM oven/QMS system. Samples are heated from 25 to 730°C under flowing He (3 ml/min) at 30 mb total pressure. Experiments consisted of reagent grade (Sigma-Aldrich) Mg(ClO₄)₂•6H₂O, and mixtures of Mg(ClO₄)₂•6H₂O (~1 mg) plus Mauna Kea palagonite HWMK919 (3.0mg) and Mg(ClO₄)₂•6H₂O (0.7 mg) plus fayalite/magnetite (Wards, Quebec) (0.7 mg) were evaluated in this work. The HWMK919 material consists plagioclase feldspar, minor pyroxene, magnetite, minor hematite, basaltic glass, allopahane, and nanophase ferric oxide [9].

Results and Discussion: The O₂ peak temperatures are ~315 and 385°C for CB and RN, respectively (Fig. 1) suggesting differing O₂ producing species for each material. John Klein has two O₂ peaks at ~225 and 370°C (Fig. 1), which suggests the presence of two O₂ evolving species. The dip between the two JK peaks could be also be attributed to consumption of O₂ during organic combustion, or thermal oxidation of a ferrous phase (e.g., magnetite to maghemite transition) [2].

The HCl temperature release characteristics from CB were different than JK and RN. Cumberland was marked by two HCl peaks at ~350 and ~730°C, with what appears to be subtle peak at ~560°C. The RN and JK possessed a gradual HCl release that peaked near ~760°C (Fig. 2). The first HCl phase in CB is coincident with the O₂ release indicating that HCl is sourced from an oxychlorine species like perchlorate or chlorate (Figs. 1,2) [2]. The second CB HCl peak and John Klein and RN peak HCl releases do not coincide with peak O₂ releases.

The thermal decomposition of Mg-perchlorate is characterized by two O₂ release peaks at 456 and 526°C, which occur at higher temperatures than the Gale Crater O₂ peaks (Fig. 1). The mixing of the fayalite/magnetite with Mg-perchlorate had no effect on

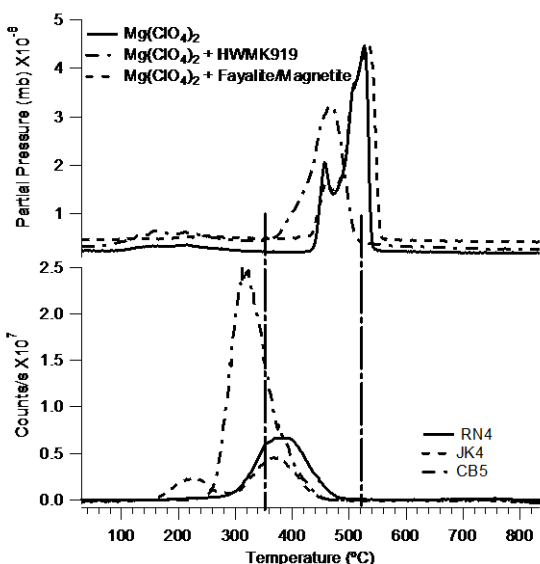


Fig. 1. O_2 release data from the thermal decomposition of a). Mg -perchlorate [$Mg(ClO_4)_2$] and ($Mg(ClO_4)_2$ +Fe phase mixtures and b). Gale Crater materials Rocknest-4 (RN4), John Klein-4 (JK4) and Cumberland-5 (CB5). Dashed-dot vertical lines indicate where the HWMK919 mixture O_2 release occurs relative to the Gale Crater O_2 releases.

reducing the thermal decomposition of Mg -perchlorate (Fig. 1).

Mixing HWMK919 with Mg -perchlorate does reduce the peak O_2 release temperature by $60^\circ C$ down to $466^\circ C$ (Fig. 1). The HWMK919 also has the effect of reducing the first lower intensity O_2 peak which results in the HWMK919 mixture having a broad O_2 release. While the O_2 peak for the HWMK 919 mixture does not coincide with the any of the Gale Crater O_2 peaks, the overall O_2 release does overlap with the last half of the Rocknest and 2nd John Klein O_2 releases (Fig. 1). This O_2 overlap suggests that Fe phases mixed with Mg -perchlorate may partly explain the O_2 releases from at least Rocknest and possibly the second John Klein peak. The possibility exists that O_2 could be sourced from reactions of Mg -perchlorate with other Fe phases in Gale Crater materials that have yet to be examined.

The Mg -perchlorate mixtures examined here suggest that some of the CB HCl could be derived from Mg -perchlorate (Fig. 2). No clear HCl contributions from Mg -perchlorate in RN or JK were observed. The HCl release peaks from Mg -perchlorate and Mg -perchlorate+fayalite/magnetite occur at $\sim 530^\circ C$ with Mg -perchlorate+HWMK919 peak at $\sim 470^\circ C$ (Fig. 2). These peaks are well below the RN and JK peaks but occur between the CB peaks (Fig. 2). The broad nature of the CB O_2 release between the two main peaks along with the subtle peak at $\sim 560^\circ C$ indicate that

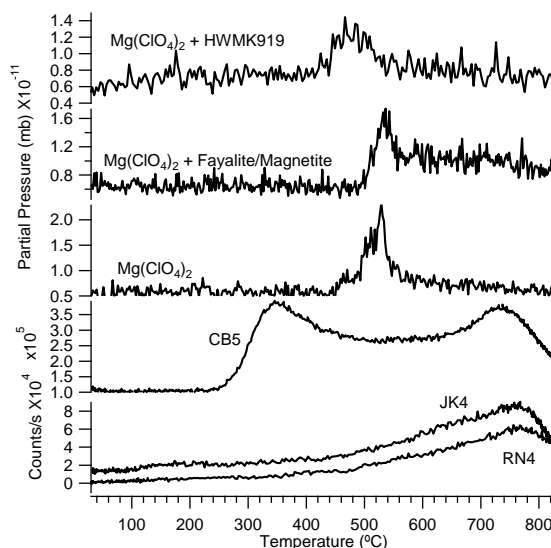


Fig. 2. HCl release data from the thermal decomposition of a). Mg -perchlorate ($Mg(ClO_4)_2$ +HWMK919, b) $Mg(ClO_4)_2$ +Fayalite/magnetite, c) $Mg(ClO_4)_2$ d). Cumberland-5 (CB5), and Rocknest-4 (RN4), John Klein-4 (JK4).

multiple HCl releases may be possible in CB suggesting that Mg -perchlorate may contribute to some of the HCl released from CB.

Mg -perchlorate may provide some O_2 and HCl due to overlapping temperatures of O_2 and HCl releases between the Gale Crater materials and the Mg -perchlorate+Fe-phases mixtures. The Mg -perchlorate and corresponding Fe-phases mixtures examined here; however, did not appear to provide ideal matches to the O_2 and HCl releases from the Gale Crater materials. Additional Fe-phases that occur in the Gale Crater materials (e.g., ilmenite, pyrite, pyrrhotite, hematite, magnetite) that have yet to be mixed with Mg -perchlorate will be analyzed to determine if improved matches of O_2 and HCl release temperatures with Gale Crater materials can be obtained.

References: [1]Leshin et al. (2013) *Science*, 341 DOI: 10.1126/science.1238937 [2]Ming et al. (2013) *Science Express* 10.1126/science. 1245267. [3]Glavin et al. (2013) *JGR*, 118,1955. [4]Glavin et al. (2013) *LPS XLV*. [5] Hecht et al. (2009) *Science*, 325, 64. [6] Markowitz, M.M. and Boryta, D.A. (1965) *J. Phys. Chem.* 69, 1114. [7] Furuichi R. et al. (1974) *J. Therm Anal.* 6,305. [8] Bruck et al. (2013) *LPS XLV*. [9] Morris et al. (2001), *JGR*, 106, 5057.